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Short communication

Enzyme-catalyzed biocathode in a photoelectrochemical biofuel cell

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HIGHLIGHTS

- A novel double-enzyme photoelectrochemical biofuel cell is developed.
- Glucose dehydrogenase and horseradish peroxidase are used as catalysts.
- Horseradish peroxidase is an efficient catalyst for the biocathode.

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ABSTRACT

A novel double-enzyme photoelectrochemical biofuel cell (PEBFC) has been developed by taking glucose dehydrogenase (GDH) and horseradish peroxidase (HRP) as the enzyme of the photoanode and biocathode to catalyze the oxidation of glucose and the reduction of oxygen. A H_2-mesoporphyrin IX is used as a dye for a TiO_2 film electrode to fabricate a photoanode. The horseradish peroxidase (HRP) is immobilized on a glassy carbon (GC) electrode to construct a biocathode which is used to catalyze the reduction of oxygen in the PEBFC for the first time. The biocathode exhibits excellent electrocatalytic activity in the presence of O_2. The performances of the PEBFC are obtained by current–voltage and power-voltage curves. The short-circuit current density (I_{sc}), the open-circuit voltage (V_{oc}), maximum power density (P_{max}), fill factor (FF) and energy conversion efficiency (η) are 439 μA cm^{-2}, 678 mV, 79 μW cm^{-2}, 0.39 and 0.016%, respectively, and the incident photon-to-collected electron conversion efficiency (IPCE) is 32% at 350 nm. The I_{sc} is higher than that of the PEBFC with Pt cathode, and the V_{oc} is higher than that of the dye-sensitized solar cell or the enzyme-catalyzed biofuel cell operating individually, which demonstrates that the HRP is an efficient catalyst for the biocathode in the PEBFC.

1. Introduction

Photoelectrochemical biofuel cells (PEBFCs) are enjoying growth in interest due to the conversion of the solar and chemical energy into electric energy [1] by combining a dye-sensitized solar cell (DSSC) [2–7] with an enzyme-catalyzed biofuel cell (BFC) [8–14]. The dye of the PEBFC (Fig. 1), depending upon photon absorption, is excited to eject electrons into the conduction band of TiO_2 and then the produced oxidized dye molecule is reduced back to its initial state by a redox mediator β-nicotinamide adenine dinucleotide reduced form disodium salt (NADH) [15–23]. The NADH is changed to the β-nicotinamide adenine dinucleotide (NAD^+) which is used as an electron acceptor to accept the electron from the oxidation of glucose by enzyme as a catalyst. The electrons ejected into the conduction band of TiO_2 are transported to the cathode by an external circuit. At the cathode, the dissolved oxygen is reduced to water. The PEBFC has been evaluated with several fuels and the corresponding enzymes, for the fuels, such as glucose, glucose-6-phosphate, methanol and ethanol. The dye-sensitized semiconductor photoanode typically employs TiO_2 rather than SnO_2 due to the wide band gap of TiO_2. Typical dyes that have been investigated include 5-(4-carboxyphenyl)-10, 15, 20-tris(4-methylphenyl) porphyrin and chlorophyll. In addition, the effect of the dye on the cell performance and [FeFe]-hydrogenase-catalyzed H_2 production

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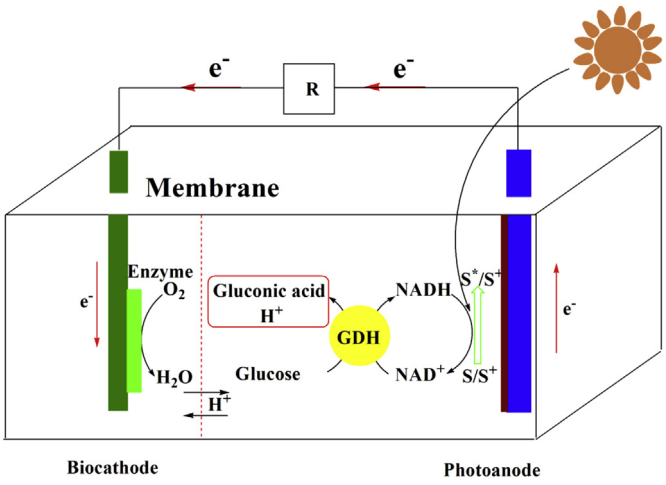

Fig. 1. Schematic diagram of the oxidation-reduction for the photoelectrochemical biofuel cell.

in the PEBFC have been deeply researched. Although the PEBFC has been extensively reported, most of the PEBFCs are utilizing extremely expensive and hardly compatible platinum (Pt) cathode to reduce oxygen. Using enzymatic catalysis in cathode is advantageous to compatibility with biocatalysts employed in the enzymatic photoanode, which usually requires the neutral or near neutral solution and low ionic strength. As a result, there is interest in using low-cost enzymes as substitutes for Pt in oxygen reduction for the PEBFC. In this paper, the horseradish peroxidase (HRP) was used as enzyme in the biocathode to catalyze oxygen reduction reaction (ORR). HRP is one of the prevalent enzymes due to its important applications in life sciences [24–28]. Furthermore, it has a great potential in enzymatic biofuel cells. Although HRP has been intensively studied with electrochemical methods [24–28], it has never been used in the PEBFC. HRP has a heme center in the polypeptide chains, so it is able to reduce O_2. Chitosan, an N-deacetylated derivative of chitin, is a natural biopolymer found in the exoskeleton of crustaceans, fungal cell wall and other biological materials. Chitosan has been applied extensively in the enzyme immobilization due to its transparency.

In this paper, chitosan was used as an enzyme support to get an enzyme with high activity. The prepared biocathode and the photoanode sensitized by H_2-mesoporphyrin IX were used to construct a PEBFC, and its performance was characterized. The short-circuit current is higher than that of the PEBFC with Pt cathode. In addition, the performances of the PEBFC employing HRP as the catalyst are much better than those of both enzymatic biofuel cell and H_2-mesoporphyrin IX sensitized solar cell under similar conditions.

2. Experimental

2.1. Materials

H_2-mesoporphyrin IX was purchased from J&K CHEMICAL LTD. β-NADH, HRP and chitosan were purchased from Sigma–Aldrich Company. Perfluorinated sulfonic acid proton-exchange membrane (Nafion 117, thickness: 80 μm, exchange capacity: 1.0 ± 0.02 mM g^{-1}) was purchased from Shandong Dongyue Shenzhou New Material Co, Shandong China. The trishydroxylaminomethane (Tris) was obtained from J&K Chemical Ltd. GDH was obtained from Toyobo Co., Ltd. The enzyme activity was assayed following a protocol provided by the manufacturer. β-D-glucose, ethanol, acetic acid, NaH_2PO_4, Na_2HPO_4, KCl and multi-walled carbon nanotubes (MWNTs) were obtained from Beijing Chemical Company (Beijing, China). 3α, 7α-dihyroxy-5β-cholic acid (cheno) was obtained from Fluka. One unit of GDH activity is defined as the amount of enzyme consumed per minute that reduced 1.0 mmol NAD^+ to NADH by glucose.

2.2. Preparation of TiO_2 film electrode

The TiO_2 film electrode was obtained from Peng Wang group in Changchun Institute of Applied Chemistry [29].

2.3. Preparation of enzyme-catalyzed biocathode

The biocathode was prepared in one pot by adsorption of enzyme (HRP) and mediator (chitosan and MWNTs) on the glassy carbon (GC) electrode. By dissolving chitosan in 2% acetic acid solution and then stirring for 2 h, 1% chitosan solution was prepared. 2 mg MWNTs and 1 mL of 1% chitosan solution were mixed together under ultrasonic condition. Then, 10 mg HRP was dissolved in 1 mL of phosphate buffer solution (PBS) solution (pH 7.0). 0.8 mL of viscous MWNTs and chitosan suspension was mixed thoroughly with 0.2 mL of HRP solution. GC electrode with 4 mm diameter was polished with 0.5 and 0.03 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for one minute, respectively. 5 μL MWNTs, chitosan and HRP suspension was spread evenly by a micropipette onto the GC electrode surface, and the electrode was covered with a small beaker and allowed to dry for over 24 h at 4 °C. Finally the biocathode containing HRP, MWNTs and chitosan was obtained.

2.4. Electrochemical measurements

All the electrochemical measurements were performed with an EG & G PARC potentiostat/galvanostat (Model 273A Princeton Applied Research Co., USA) and a conventional three compartment electrochemical cell. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All potentials were referenced to SCE. The biocathode prepared according to 2.3 was used as working electrode.

2.5. Fabrication of photoelectrochemical biofuel cell

The detailed fabrication procedures of the photoanode FTO/TiO_2/H_2- mesoporphyrin IX and the PEBFC have been reported in the previous literature [24]. The photoanode compartment was filled with 4 mM NADH, 0.1 M glucose, 0.015 U mL^{-1} GDH and 0.25 M Tris buffer solution with pH 7.0 (adjusted with HCl) that contained 0.1 M KCl as a supporting electrolyte. To remove oxygen, the photoanode compartment was saturated by nitrogen gas. The biocathode compartment was filled with 0.1 M KCl and 0.25 M Tris buffer solution of pH 7.0 with saturated oxygen.

2.6. Photovoltaic characteristics

A Keithley 2400 source meter and a Zolix Omni-l300 monochromator equipped with a 500 W xenon lamp were used for photocurrent action spectrum measurements with a wavelength sampling interval of 10 nm and a current sampling interval of 2 s under computer control. A Hamamatsu S1337-1010BQ silicon diode used for IPCE measurements was calibrated at the National Institute of Metrology, China. A model LS1000-4S-AM1.5G-1000 W solar simulator (Solar Light Co., Glenside, PA) was employed to give an irradiance of 100 mW cm^{-2}. The light intensity was tested with a PMA2144 pyranometer and calibrated with PMA 2100 dose control system. The current–voltage characteristics were measured with a

Keithley 2602 source meter under computer control. The measurements were fully automated using Labview 8.0 (USA) [29].

3. Results and discussion

3.1. The reaction mechanism of photoelectrochemical biofuel cell

The PEBFC relies upon charge separation at a dye-sensitized TiO_2 semiconductor film photoanode. The dye is excited by visible light, resulting in electron ejection from the excited dye into the conduction band of TiO_2; these electrons are collected at the FTO conductive glass. The above process is summarized as follows:

$$\text{dye} + h\nu \rightarrow \text{dye}^* \quad (1)$$

$$\text{dye}^* \rightarrow \text{dye}^+ + e^-(TiO_2) \quad (2)$$

$$e^-(TiO_2) \rightarrow e^-(FTO) \quad (3)$$

The photoanode half-cell compartment contains GDH as a biocatalyst and $NADH/NAD^+$ as a redox mediator. The produced dye in oxidized state (dye^+) oxidizes the NADH to the NAD^+ which can be served as an electron acceptor; glucose under the catalysis of GDH gives electrons to NAD^+, which regenerates NADH. The above process is summarized as follows:

$$\text{dye}^+ + e^-(\text{from NADH}) \rightarrow \text{dye(dye regeneration)} + NAD^+ \quad (4)$$

$$\text{Glucose} \xrightarrow{\text{GDH}} \text{gluconolactone} + 2e^- + 2H^+ \quad (5)$$

$$NAD^+ + 2e^- + H^+ \rightarrow \text{NADH(NADH regeneration)} \quad (6)$$

The electrons collected at the FTO conductive glass are transported to the cathode by an external circuit. In the previous reports, the photoanode is coupled with a Pt cathode and the dissolved oxygen is reduced to water by Pt as a catalyst for O_2 reduction reaction (ORR). In this work, HRP as low-cost and high performance catalyst for ORR at the cathode is used for the first time in the PEBFC. The reaction is

$$O_2 + 4e^- + 4H^+ \xrightarrow{\text{HRP}} 2H_2O \quad (7)$$

Therefore, the total reaction in PEBFC is

$$\text{Glucose} + \frac{1}{2}O_2 \xrightarrow{h\nu} \text{gluconolactone} + H_2O \quad (8)$$

3.2. Effect of scan rate on direct electron transfer of HRP

The effect of scan rate on the current-potential response of immobilized HRP is shown in Fig. 2. With the increase of scan rate, the redox peak currents also increase gradually. The relationship of the redox peak current with the scan rate is shown in Fig. 3. The linear regression equations were $i_{pa} = 49.622v + 0.5295$ (μA, V s^{-1}, $R^2 = 0.9991$), $i_{pc} = -75.679$ v−1.8116 (μA, V s^{-1}, $R^2 = 0.9997$), indicating that the electrode reaction was a typical of surface-controlled quasireversible process.

3.3. ORR Performance

Cyclic voltammetry was used to study the electrocatalytic behavior at the biocathode. Fig. 4 shows the cyclic voltammograms

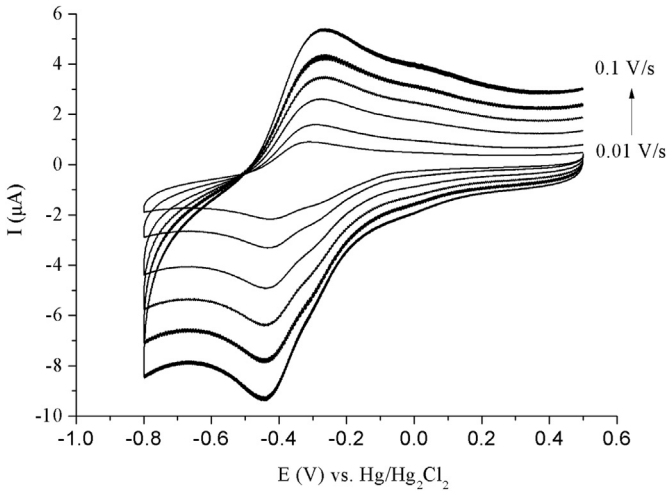

Fig. 2. Cyclic voltammograms at the GC electrode modified with HRP/CNTs/Chi film in 0.2 M PBS (pH 7.0) at different scan rates: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 V s^{-1} (from inner to outer).

at the biocathode in the presence of O_2 or N_2 in 0.1 M PBS (pH 7.0) at a scan rate of 0.2 V s^{-1}. It can be seen that the cathodic currents was remarkably enhanced due to presence of O_2, indicating electrocatalysis for the reduction reaction of O_2.

3.4. Photocurrent action spectrum

To evaluate the performance of the biocathode, the photocurrent action spectrum for PEBFC with biocathode is shown in Fig. 5. The absorption peaks in the photocurrent action spectrum are observed at 350, 438, 516 and 660 nm, and the corresponding IPCEs are ca. 32%, 12%, 9% and 3%, respectively.

The light-harvesting efficiency (LHE) at any particular wavelength is calculated by formulas $1-10^{-A}$, where A is the absorbance. The LHE curve of TiO_2 film electrode sensitized by TCPP is shown in Fig. 5. There are some similarities between the IPCE and LHE curves. For example, at near 347, 438, 520 and 654 nm, photons can be trapped, and the photogenerated electrons can be ejected into the external circuit of the PEBFC (Fig. 5).

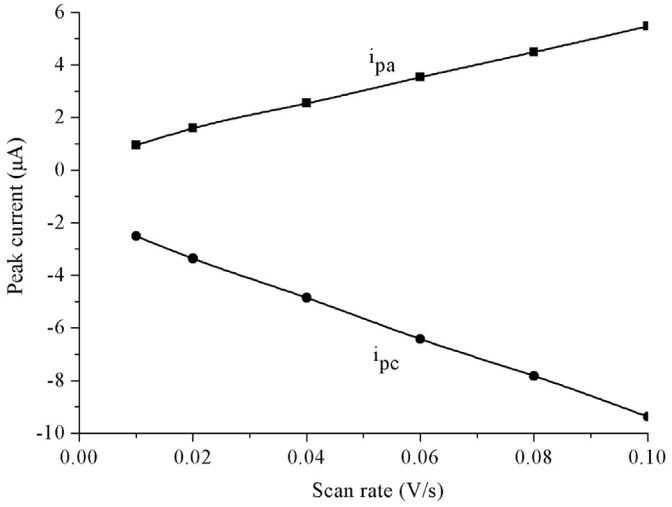

Fig. 3. The plot of peak current vs. scan rates.

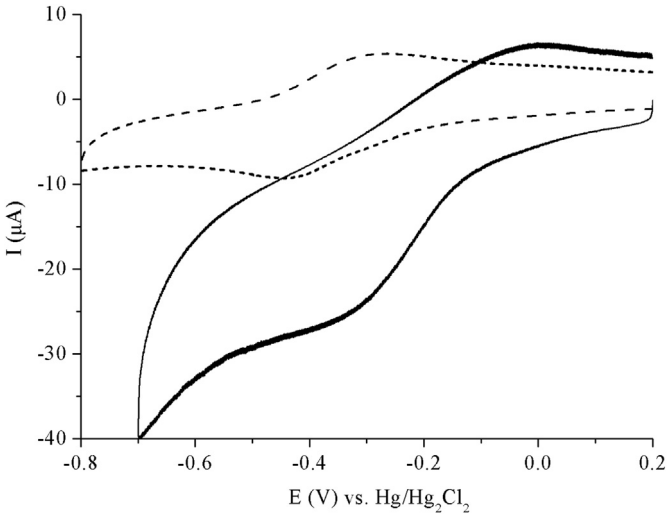

Fig. 4. Cyclic voltammograms at the GC electrode modified with HRP/CNTs/Chi film in 0.2 M PBS (pH 7.0) saturated with O_2 (solid line) or N_2 (dashed line) at scanning rate of 0.2 V s^{-1}.

3.5. Performance of the PEBFC

The performance of the PEBFC with the biocathode was investigated by current–voltage and power-voltage curves as shown in Fig. 6. The PEBFC generated the short-circuit current (I_{sc}), the open-circuit voltage (V_{oc}), maximum power density (P_{max}), fill factor (FF) and energy conversion efficiency (η) were 100 μA (corresponding to 439 μA cm^{-2}, according to the geometrical area of the TiO_2 film electrode), 678 mV, 79 μW cm^{-2}, 0.39 and 0.016%, respectively. We constructed the H_2-mesoporphyrin IX sensitized PEBFC with Pt cathode for oxygen reduction [23]. The control current–voltage characteristics for the PEBFCs with the HRP biocathode and Pt cathode have been used to evaluate the comparative performances as shown in Fig. 7. The I_{sc} of the PEBFC with the HRP biocathode is higher than that (I_{sc} = 90 μA) of the PEBFC with Pt cathode, which may stem from the higher efficiency of HRP enzyme. The P_{max} is greater than that of the glucose/O_2 biofuel cells under similar conditions in previous studies such as 1.12 μW cm^{-2} [30], 8 μW cm^{-2} [31], 5.49 μW cm^{-2} and 16 μW cm^{-2} [32–37], and the V_{oc} is greater than that (V_{oc} = 400 mV) of the glucose biofuel cell as shown in Table 1. Therefore, the PEBFC can operate at a higher voltage than the BFC with the same fuel and the same ORR cathodic

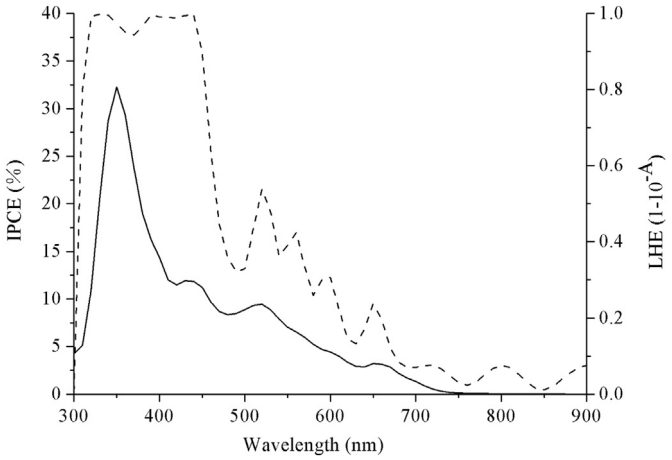

Fig. 5. Photocurrent action spectrum (solid line) and light-harvesting efficiency (dashed line) for the photoelectrochemical biofuel cell.

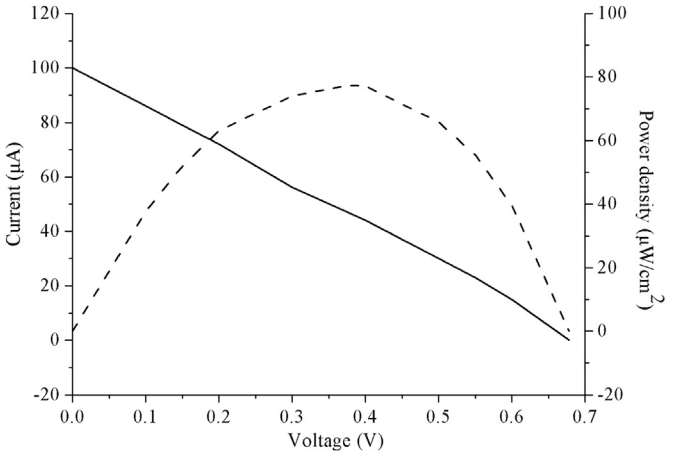

Fig. 6. Current–voltage (solid line) and power-voltage (dashed line) characteristics for the PEBFC with the biocathode.

half-cell. Grätzel et al. reported that the DSSC sensitized by H_2-mesoporphyrin IX exhibited 520 mV V_{oc} [38], and the V_{oc} value is lower than that of the PEBFC sensitized by H_2-mesoporphyrin IX (Table 1). Thus the PEBFC can operate at a higher voltage than the DSSC using the same semiconductor and dye. So, the performances of the PEBFC are better than those of both enzymatic biofuel cell and H_2-mesoporphyrin IX sensitized solar cell for V_{oc} value. However, the efficiency demonstrated by the PEBFC is still very low compared with that of the DSSC as shown in Table 1, the PEBFC may be commercialized after the performance of the PEBFC is improved.

Next let us focus on the long-time stability of the PEBFC against continuous irradiation. After 24 h irradiation with the light

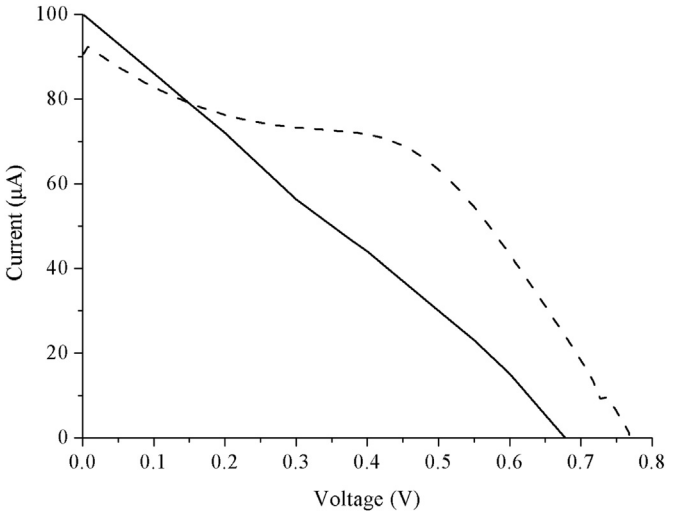

Fig. 7. Current–voltage characteristics for the PEBFCs with the HRP biocathode (solid line) and Pt cathode (dashed line).

Table 1
The performance comparation for the PEBFC, the glucose/O_2 BFC and the DSSC sensitized by H_2-mesoporphyrin IX.

	PEBFC	Glucose/O_2 BFC	DSSC sensitized by H_2-mesoporphyrin IX
V_{oc} (mV)	678	400	520
P_{max} (μW cm^{-2})	79	16	78
η	0.016%	/	2.6%

intensity of 100 mW cm^{-2} xenon lamp, only little current and voltage changes are observed (±5.0%), indicating that the PEBFC is stable against irradiation within 24 h irradiation.

4. Conclusions

This is the first report on the double-enzyme photoelectrochemical biofuel cell that utilizes biocatalysts in both photoanode and cathode compartments. The most important point is utilization of the horseradish peroxidase to reduce O_2 to H_2O in the cathodic half-cell. The PEBFC based on the HRP biocathode generates higher I_{sc} than that with Pt cathode. The PEBFC can offer higher open-circuit voltage over either the dye-sensitized solar cell or the enzyme-catalyzed biofuel cell alone. Therefore, HRP as a novel catalyst of O_2 reduction reaction is very efficient for the PEBFC.

Acknowledgments

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